Physics 460/560 Lecture 1

Electrons in Metals II

• 3D Fermi gas: Ground state

The ground state of a spin-1/2 Fermi gas in three dimensions is

$$|\Psi_0\rangle = \prod_{\sigma=\uparrow,\downarrow} \prod_{|\vec{k}|\leq k_F} c^{\dagger}_{\vec{k}\sigma} |0\rangle,$$

where k_F is a cutoff known as the <u>Fermi wavevector</u>. Important physical systems, such as electrons in metals, neutrons in a neutron star, etc., can be described by such a Fermi gas.

- **Boundary conditions** Let N Fermions occupy a cube of volume $L^3 = V$. Impose periodic boundary conditions:

$$\psi_{\vec{k}}(x+L, y, z) = \psi_{\vec{k}}(x, y+L, z) = \psi_{\vec{k}}(x, y, z+L)$$

$$= \psi_{\vec{k}}(x, y, z).$$

- $$\psi_{\vec{k}}(x, y, z) = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{x}} = \frac{1}{\sqrt{V}} e^{ik_x x} e^{ik_y y} e^{ik_z z}$$

$$\Longrightarrow \quad \vec{k} = \frac{2\pi}{L}\vec{n}, \qquad n_i \in \mathbb{Z}$$

These are the allowed wavevectors, subject to periodic boundary conditions. The energy of a particle is

- $$\mathcal{E}_{\vec{k}} = \frac{\hbar^2 \vec{k}^2}{2m}.$$

Total # of particles

$$N = \sum_{\sigma=\uparrow}^{\downarrow} \sum_{\vec{k}} \theta(k_F - |\vec{k}|) = 2 \sum_{\vec{k}} \theta(k_F - |\vec{k}|)$$

$$= 2 \int d^3n \; \theta(k_F - |\vec{k}|)$$

$$= 2 \left(\frac{L}{2\pi}\right)^3 \int d^3k \; \theta(k_F - |\vec{k}|)$$

$$= \frac{V}{4\pi^3} \frac{4}{3}\pi k_F{}^3 = \frac{V k_F{}^3}{3\pi^2}$$

$$\rho = \frac{N}{V} = \frac{k_F{}^3}{3\pi^2}$$

$$\boxed{k_F = \left(3\pi^2 \frac{N}{V}\right)^{1/3}} \quad \text{Fermi wavevector}$$

Fermi energy

- The energy of the highest occupied state is

$$\varepsilon_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}.$$

Fermi velocity

A particle at the Fermi energy

- travels at a speed

$$V_F = \frac{\hbar k_F}{m} = \frac{\hbar}{m}\left(3\pi^2\frac{N}{V}\right)^{1/3}.$$

Total energy

$$E = 2\sum_{\vec{k}} \varepsilon_{\vec{k}} = 2\left(\frac{L}{2\pi}\right)^3 \int_{|\vec{k}|\le k_F} d^3k\, \frac{\hbar^2 \vec{k}^2}{2m}$$

- $$= \frac{V}{\pi^2}\frac{\hbar^2}{2m}\int_0^{k_F} k^4\, dk = \frac{V k_F^3}{5\pi^2}\frac{\hbar^2 k_F^2}{2m}$$

$$\boxed{E = \frac{3}{5} N \varepsilon_F}$$

The average energy per particle in the ground state of a Fermi gas is $\frac{3}{5}$ of the Fermi energy!

Typical Fermi gas parameters are exhibited by Copper:

V_F	ε_F	$T_F = \varepsilon_F / k_B$
1.56×10^3 km/s	7.0 eV	8.2×10^4 K
$\sim \frac{c}{200}$		

Typical conduction electron in copper is zipping around at $\frac{1}{2}$% the speed of light!

Fermi Pressure

$$P = -\left.\frac{\partial E}{\partial V}\right|_{N,S} \qquad (S=0 \text{ at } T=0)$$

$$E = \frac{3}{5} N \varepsilon_F = \frac{3\hbar^2}{10m} N \left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

$$P = -\left.\frac{\partial E}{\partial V}\right|_{N,S} = \frac{\hbar^2}{5m} \frac{N}{V} \left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

$$\boxed{P = \frac{2}{5} \frac{N}{V} \varepsilon_F}$$

In copper, one has

$$P_{Cu} = \frac{2}{5} \rho \, \mathcal{E}_F = 0.4\left(8.5\times10^{22}\,\text{cm}^{-3}\right) 7.0\,\text{eV}$$

$$= 1.1\times10^{11}\,\text{N/m}^2 \approx 10^6\ \text{Atm} \ !$$

The Fermi pressure exerts a repulsive force equivalent to one million atmospheres of pressure!

Q: why doesn't a penny fly apart under this tremendous pressure?

A: The repulsive force from the Fermi pressure is balanced by an equally strong attractive force between the negatively charged electrons and the positive ions.

Bulk modulus

Although the Fermi pressure is not directly measurable since it is in balance with the Coulomb forces, the Bulk modulus, which characterizes the compressibility of a solid, is measurable:

$$B = -V \frac{\partial P}{\partial V} = \frac{\hbar^2}{3m} \frac{N}{V} \left(\frac{3\pi^2 N}{V} \right)^{2/3}$$

$$B = \frac{5}{3} P.$$

Bulk moduli (10^{10} Dynes/cm^2)

metal	Free electron B	measured B
Li	23.9	11.5
Na	9.23	6.42
K	3.19	2.81
Rb	2.28	1.92
Cs	1.54	1.43
Cu	63.8	134.3
Ag	34.5	99.9

The bulk moduli of the heavier alkali metals are rather well described by the free electron model. The discrepancy can be explained to some extent by the fact that the interaction of an electron with the lattice tends to increase its effective mass, decreasing the bulk modulus.

However, in the noble metals, the bulk modulus significantly exceeds the free electron value. This is a sign that the ionic core electrons play an important role in the noble metals. They give an additional repulsive contribution to B.

$T > 0$: The Fermi-Dirac Distribution

A Fermionic state $\vec{k}\sigma$ with energy $\varepsilon_{\vec{k}}$ may be empty, or filled with one fermion. The grand partition function of the state is

$$\mathcal{Z} = 1 + e^{-\beta(\varepsilon_{\vec{k}} - \mu)}.$$

The probability that the state is empty is

$$p = \frac{1}{\mathcal{Z}}.$$

The probability that it is occupied is

$$p = \frac{e^{-\beta(\varepsilon_{\vec{k}} - \mu)}}{Z}.$$

The average # of Fermions in this state is thus

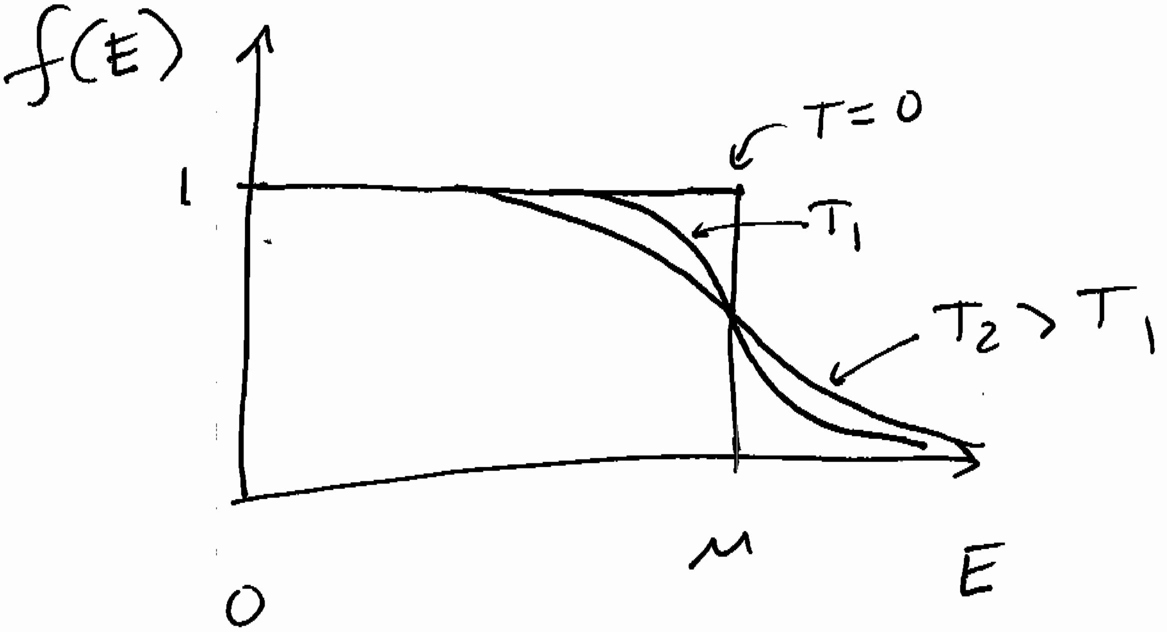
$$\langle n_{\vec{k}\sigma} \rangle = \frac{e^{-\beta(\varepsilon_{\vec{k}} - \mu)}}{1 + e^{-\beta(\varepsilon_{\vec{k}} - \mu)}}$$

$$= \frac{1}{e^{\beta(\varepsilon_{\vec{k}} - \mu)} + 1}$$

$$\boxed{f(E) = \frac{1}{e^{\beta(E-\mu)} + 1} \quad \text{Fermi-Dirac distribution}}$$

The chemical potential μ is determined by fixing the total # of particles:

$$N = \sum_{\vec{k}\sigma} \langle n_{\vec{k}\sigma} \rangle = 2V \int \frac{d^3k}{(2\pi)^3} f(E_{\vec{k}})$$



$$\lim_{T \to 0} f(E) = \theta(\mu - E)$$

$$\lim_{T \to 0} \mu(T) = \varepsilon_F$$

Heat capacity

$$C_V = \frac{\partial E}{\partial T}\Big|_V$$

$$E = 2 \sum_{\vec{k}} \varepsilon_{\vec{k}} \, f(\varepsilon_{\vec{k}})$$

$$= 2V \int \frac{d^3k}{(2\pi)^3} \varepsilon_{\vec{k}} \, f(\varepsilon_{\vec{k}})$$

$$\equiv \int d\varepsilon \, \varepsilon \, f(\varepsilon) \, D(\varepsilon),$$

where $D(\varepsilon)$ = <u>density of states</u>

$$\frac{V}{4\pi^3} d^3k = \frac{V}{\pi^2} k^2 dk = \frac{V}{\pi^2} \frac{2m\varepsilon}{\hbar^2} \frac{d\varepsilon}{\frac{d\varepsilon}{dk}}$$

$$\Rightarrow D(\varepsilon) = \frac{V}{\pi^2} \frac{2m\varepsilon}{\hbar^2} \frac{1}{\frac{d\varepsilon}{dk}}$$

$$\frac{d\varepsilon}{dk} = \frac{\hbar^2 k}{m} = \frac{\hbar}{m}\sqrt{2mE}$$

$$\boxed{D(\varepsilon) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \varepsilon^{1/2}}$$

for spin-1/2 in volume V.

This result can also be derived by considering the # of states $N(E)$ with energy $\leq E$:

$$N(E) = 2V\int \frac{d^3k}{(2\pi)^3}\, \theta\left(\sqrt{\frac{2mE}{\hbar^2}} - |\vec{k}|\right)$$

$$= \frac{V}{4\pi^3} \frac{4}{3}\pi \left(\frac{2mE}{\hbar^2}\right)^{3/2}$$

$$N(E) = \frac{V}{3\pi^2}\left(\frac{2mE}{\hbar^2}\right)^{3/2}$$

$$D(E) = \frac{dN(E)}{dE} = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$$

Now back to calculating C_V:

$$C_V = \int_0^\infty d\varepsilon \;\; \varepsilon\, D(\varepsilon)\, \frac{\partial f}{\partial T}(\varepsilon)$$

now, $\displaystyle \frac{\partial f}{\partial T} = \frac{\partial f}{\partial \beta}\frac{\partial \beta}{\partial T} = -\frac{1}{k_B T^2}\frac{\partial f}{\partial \beta}$

$$\frac{\partial f}{\partial T} = \frac{1}{k_B T^2}\frac{(E-\mu)\, e^{\beta(E-\mu)}}{\left(e^{\beta(E-\mu)}+1\right)^2}$$

But $\frac{\partial f}{\partial E} = -\beta \frac{e^{\beta(E-\mu)}}{\left(e^{\beta(E-\mu)}+1\right)^2}$

so $\frac{\partial f}{\partial T} = \frac{E-\mu}{T}\left(-\frac{\partial f}{\partial E}\right)$.

$-\frac{\partial f}{\partial E}$ is everywhere positive, and is sharply peaked around $E=\mu$ for $k_B T \ll \varepsilon_F$.

(Recall that $\frac{\varepsilon_F}{k_B} \sim 10^4 K$, so even at room temperature, $k_B T \ll \varepsilon_F$.)

$$C_V = \int_0^\infty d\varepsilon \; \varepsilon \, D(\varepsilon) \, \frac{\varepsilon - \mu}{T} \left(-\frac{\partial f}{\partial \varepsilon} \right)$$

$$= \frac{1}{k_B T^2} \int_0^\infty d\varepsilon \, \frac{\varepsilon \, D(\varepsilon)(\varepsilon - \mu)}{\left(e^{\frac{\beta(\varepsilon - \mu)}{2}} + e^{-\frac{\beta(\varepsilon - \mu)}{2}} \right)^2}$$

let $\beta(\varepsilon - \mu) = x$

$$C_V = k_B^2 T \int_{-\beta\mu}^\infty dx \, \frac{\left(x^2 + \beta\mu x \right) D(\mu + \frac{x}{\beta})}{\left(e^{x/2} + e^{-x/2} \right)^2}$$

The integrand is sharply peaked around $x = 0$, so we can take the lower limit $-\beta\mu \to -\infty$ for $k_B T \ll \varepsilon_F$. Also, $D(\varepsilon)$ may be pulled outside the integral as $D(\varepsilon_F)$. Thus

$$C_V \cong k_B^2 T D(\varepsilon_F) \int_{-\infty}^{\infty} dx \, \frac{x^2 + \beta\mu x}{\left(e^{\frac{x}{2}} + e^{-\frac{x}{2}}\right)^2}$$

The term linear in x in the integrand is odd, and gives zero.

$$C_V = k_B^2 T D(\varepsilon_F) \underbrace{\int_{-\infty}^{\infty} dx \, \frac{x^2}{\left(e^{\frac{x}{2}} + e^{-\frac{x}{2}}\right)^2}}_{\pi^2/3}$$

$$\boxed{C_V = \frac{\pi^2}{3} k_B^2 T D(\varepsilon_F) \quad \text{or} \quad \frac{C_V}{N k_B} = \frac{\pi^2}{2} \frac{k_B T}{\varepsilon_F}}$$

For a metal, there are 2 contributions to the specific heat at low temperatures; one from the conduction electrons, $\propto T$, and one from the phonons, $\propto T^3$:

$$\boxed{\frac{C_V}{N k_B} = \frac{\pi^2}{2} \frac{T}{T_F} + \frac{12\pi^4}{5} \left(\frac{T}{\underset{\text{Debye temp.}}{\theta_D}} \right)^3}$$

By plotting $\frac{C_V}{T}$ vs. T^2, one can extract θ_D from the slope and T_F from the intercept. Comparing to the free electron model, one finds:

Heat capacity (mJ/mol °K)

metal	Free electron C_v	measured C_v
Li	0.749	1.63
Na	1.094	1.38
K	1.668	2.08
Rb	1.911	2.41
Cs	2.238	3.20
Cu	0.505	0.695
Ag	0.645	0.646

Thus, the free electron model gives the correct order of magnitude for the linear term in the specific heat.

Again, the discrepancy in the alkali metals can be ascribed to an increased effective mass, which <u>increases</u> C_V.